

CORRECTED VERSION

**(19) World Intellectual Property Organization
International Bureau**



(43) International Publication Date
17 August 2000 (17.08.2000)

(10) International Publication Number
WO 00/48435 A1

(51) International Patent Classification⁷: H05H 1/24,
C23C 16/26

(74) Agent: SUDDERTH, D., Scott; Womble Carlyle Sandridge & Rice, PLLC, P.O. Box 725388, Atlanta, GA 31139-9388 (US).

(21) International Application Number: PCT/US00/03502

(22) International Filing Date: 10 February 2000 (10.02.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/119,771 10 February 1999 (10.02.1999) US

(71) Applicant: AUBURN UNIVERSITY [US/US]; Industrial Programs and Technology Transfer, 309 Samford Hall, Auburn University, AL 36849-5176 (US).

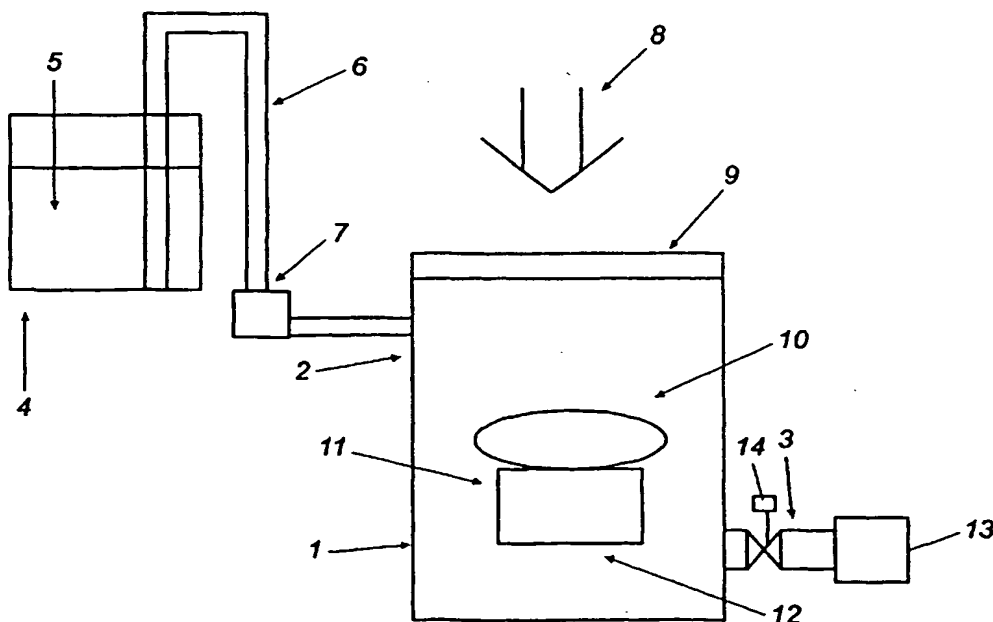
(72) Inventor: TZENG, Yonhua; 306 Graystone Lane.
Auburn, AL 36830 (US).

(81) Designated States (national): AE, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,

[Continued on next page]

(54) Title: METHOD OF PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF DIAMOND



(57) Abstract: A plasma CVD process of forming diamond crystals or a diamond film on a substrate (11) is disclosed, wherein a liquid precursor (5) comprising methanol and at least one carbon containing compound is introduced into a reaction chamber (1) through a liquid flow controller (7), and it vaporizes to form a vapor precursor. An electromagnetic discharge is applied to dissociate the vapor precursor to generate oxidizing and etching radicals as well as carbon depositing radicals.

BEST AVAILABLE COPY

WO 00/48435 A1



MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(15) Information about Correction:

see PCT Gazette No. 02/2002 of 10 January 2002, Section II .

Published:

— *with international search report*

(48) Date of publication of this corrected version:

10 January 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD OF PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF DIAMOND

This application claims benefit of U.S. Provisional Patent Application No. 60/119,771 filed February 10, 1999, incorporated herein by reference in its entirety.

5 The invention was made with support from the United States National Aeronautics and Space Administration (Contract No. NASA/NCC5-165) and the United States Department of the Navy (Contract No. Navy/N00014-98-1-0571). The Federal Government may retain certain rights in the invention.

10

FIELD OF THE INVENTION

The present invention relates to a method of synthesizing diamond. In particular, the present invention relates to a method of synthesizing diamond crystals and diamond films using plasma enhanced chemical vapor deposition.

15

BACKGROUND OF THE INVENTION

Diamond synthesized by chemical vapor deposition ("CVD") has many unique and outstanding properties that make it an ideal material a broad range of scientific and technological applications. See Y. Tzeng et al., *Application of Diamond Films And Related Materials*, Elsevier Publishers, 1991. A number of methods for diamond
20 CVD are reported which utilize various gas mixtures and energy sources for dissociating the gas mixture. See P.K. Bachmann et al., *Diamond and Related Materials* 1, 1, (1991). Such methods include the use of high temperature electrons in various kinds of plasma, high solid surfaces on hot filaments, and high temperature

gases in combustion flames to dissociate molecules such as hydrogen, oxygen, halogen, hydrocarbon, and other carbon containing gases. Typically, a diamond crystal or film is grown on a substrate, which is usually maintained at a temperature much lower than that of electrons in the plasma, the heated surface of a hot filament, or the combustion flame. As a result, a super equilibrium of atomic hydrogen is developed near the diamond growing surface of the substrate.

Atomic hydrogen is believed to be crucial in the diamond CVD process. It is theorized that atomic hydrogen is effective in stabilizing the diamond growing surface and promoting diamond growth at a CVD temperature and pressure that otherwise thermodynamically favors graphite growth. Consistently, the reported diamond CVD processes involve the use of hydrogen gas or hydrogen containing molecules. The most typical diamond CVD process utilizes a precursor comprising of methane gas diluted by 94-99% hydrogen. With these CVD processes, the super equilibrium of atomic hydrogen can be achieved at a varied percentage of molecular hydrogen in the gas mixture. However, these CVD processes depend on the effectiveness of the dissociation process in generating atomic hydrogen.

Chein et al., Proceedings of the 6th International Conference on New Diamond Science and Technology (1998), report using a high power density microwave plasma to deposit diamond in a precursor comprising of a mixture of methane and hydrogen with less than 50% hydrogen. Growth of diamond from oxy-acetylene flames utilizes a precursor comprising of acetylene and oxygen with a ratio of acetylene to oxygen slightly greater than 1 without additional molecular hydrogen being added. Diamond is deposited in the reducing "inner flame" where atomic hydrogen is a burn product

produced by the high temperature flame. In addition to atomic hydrogen, there are plenty of OH radicals present near the diamond growing surface inside the flame.

OH and O radicals can play another role of atomic hydrogen in the diamond growth process. That is, preferential etching of non-diamond carbon, which results in
5 a net deposition of high purity diamond. Small quantity of oxygen (0.5-2%) or water vapor (<6%) added to the methane and hydrogen precursor is reported to improve diamond crystallinity and lower the diamond CVD temperature. See Saito et al., Journal of Materials Science, 23, 842 (1988), and Kawato et al., J. Applied Physics, 26, 1429 (1987). The quantity, whether small or large, of oxygen and water in a
10 precursor or feedstock is a relative term depending on many other process parameters. Diamond has also been grown in a microwave plasma of a precursor comprising of an acetone/oxygen mixture with a molecular ratio near 1:1. See Chein et al., Proceedings of the 6th International Conference on New Diamond Science and Technology (I 998).

15 Most of the diamond CVD processes involve the use of one or more compressed gases. Typically, such CVD processes utilize a compressed gas precursor comprising of 1 vol.% methane gas diluted by 99 vol.% hydrogen. These gases usually must be precisely controlled by electronic mass flow controllers to ensure the accurate composition in the gas precursor feed.

20 In U.S. Patent No. 5,480,686 to Rudder et al. ("*Rudder*") a method of diamond growth is disclosed that utilizes a radio frequency ("RF") plasma in a precursor comprising of a mixture of water (more than 40%) and alcohol. No compressed gases are needed for this diamond CVD process. However, water has a low vapor pressure

at room temperature, and condensation of water in the cooler part of the reactor manifold may be a concern. Also, water has a high freezing temperature making it easy to freeze at the orifice of a flow controller where liquid vaporizes and enters a low pressure reactor chamber. Buck et al. ("*Buck*"), "Microwave CVD of diamond using methanol-rare gas mixtures," Materials Research Society Symposium Proceedings, Vol. 162, 97-102, 1989.) have grown clusters of diamond crystallites on small (2-4 mm²) silicon substrates that were scratched with a diamond tip or mechanically polished with 3 µm diamond powder by microwave plasma enhanced CVD in pure methanol vapor. Argon gas additive was found necessary for high quality diamond to be deposited in the methanol vapor. When it is fully dissociated and reacted in the plasma, the pure methanol vapor plasma contains a C/O/H composition similar to that of CO/H₂ plasma, which has been used for successful deposition of diamond by means of electrical discharges. See Ito et al., Proceedings of International Conference on New Diamond Science and Technology, p.2-16 (1988).

In a typical electrical discharge such as a microwave plasma, electrons with an average temperature exceeding 10,000°C are abundant. These energetic electrons effectively dissociate molecular species and generate a high concentration of radicals necessary for the deposition of diamond and the preferential etching of non-diamond deposits without needing a high temperature filament. Hot filament assisted CVD processes employ solid surfaces at a temperature of about 2,000° C-2,500° C to dissociate molecules and generate radicals necessary for diamond deposition. The hot filament temperature is much lower than that of energetic electrons in a plasma. As a

consequence, hot-filament CVD of diamond in CO/H₂ mixtures has not been successful even though the same gas mixtures have been routinely used for plasma assisted deposition of diamond films.

Nevertheless, the plasma enhanced CVD method is desirable because diamond
5 crystals and films can be deposited on large-area and/or irregularly shaped objects using inexpensive equipment. Thus, there remains a need for an economic method of synthesizing diamond utilizing plasma enhanced CVD. Further, there remains a need for a method of diamond CVD which preferentially etch non-diamond deposits at low substrate temperatures to provide the deposition of high quality diamond.

10 Additionally, there remains a need for a method of diamond CVD that does not require the use of compressed gases or water or precision electronic mass flow controllers. It is to the provision of a method of plasma enhanced CVD of diamond that meets these needs that the present invention is primarily directed.

SUMMARY OF THE INVENTION

Briefly described, the present invention relates to a method of synthesizing diamond that enables the economic growth of high quality diamond crystals and diamond films using a liquid solution as the feedstock and an electrical discharge as the means of dissociating and reacting the vapor of the said solution. In the method of the present invention, a precursor comprising at least one carbon containing compound having a carbon to oxygen ratio greater than one is fed into a deposition chamber through a liquid flow controller such as a needle valve. The precursor further comprises a solution of methanol and at least one carbon containing compounds having a carbon to oxygen ratio greater than one. The solution is pre-mix prior to entering the deposition chamber. Such carbon containing compounds include ethanol, isopropanol, and acetone. The solution vaporizes as it enters the low pressure deposition chamber. The vaporized precursor comprises the same composition as the solution. When the vapor passes through an electrical discharge zone, it is dissociated to generate OH, H, O, CH₃, and other molecules and radicals.

The substrate generally is sheet or wafer of silicon, copper, aluminum and molybdenum. Some of the substrates are polished using 1 μm diamond paste prior to the deposition process. Typically, the substrate is mounted on a water cooled substrate holder. The substrate can be either in touch with the plasma or at a distance from the plasma. In experiments using the method of the present invention, the substrate was in touch with a microwave plasma ball generated inside a cylindrical microwave cavity. The reactor chamber pressure generally is maintained between 1

mtorr and 250 torr. The substrate of about 25mm x 25mm was heated by the plasma to about 300-1600°C. Diamond is deposited at a rate of 0.05-20 μm per hour depending on the composition of the solution, the vapor pressure, the substrate temperature, and the plasma power density.

5 Various other objects, features and advantages of the present invention will become known to those skilled in the art upon reading the following specification when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a microwave plasma enhanced chemical
10 vapor deposition system made in accordance with the present invention.

Figure 2 is an optical micrograph of a free-standing diamond film deposited in accordance with the present invention on a molybdenum substrate by a microwave plasma in the vapor of a precursor solution comprising 4.6 grams of ethanol and 100 grams of methanol.

15 Figure 3 is a graphic illustration of a Raman spectrum for the diamond film of Figure 2.

Figure 4 is an optical micrograph of a diamond film deposited in accordance with the present invention on silicon by a microwave plasma in the vapor of a precursor solution comprising 4 grams of isopropanol and 100 grams of methanol.

20 Figure 5 is a graphic illustration of a Raman spectrum for the diamond film of Figure 4.

Figure 6 is an optical micrograph of a free-standing diamond film deposited in accordance with the present invention on a molybdenum substrate by a microwave

plasma in the vapor of a precursor solution comprising 3.5 grams of acetone and 100 grams of methanol.

Figure 7 is a graphic illustration of a Raman spectrum for the diamond film of Figure 6.

5 Figure 8 is an optical micrograph of a diamond film deposited in accordance with the present invention on an aluminum plate by a microwave plasma in the vapor of a precursor solution comprising 15 grams of acetone and 100 grams of methanol.

Figure 9 is a graphic illustration of a Raman spectrum for the diamond film of Figure 8.

10 Figure 10 is an optical micrograph of diamond crystallites grown in accordance with the present invention on a clean and untreated silicon wafer by a microwave plasma in the vapor of a precursor solution comprising 50 grams of acetone and 100 grams of methanol.

Figure 11 is a graphic illustration of a Raman spectrum for a diamond
15 crystallite of Figure 10.

Figure 12 is an optical micrograph of a diamond film deposited in accordance with the present invention on a clean and scratched (by diamond paste with 1 μm diamond powder) silicon wafer by a microwave plasma in the vapor of a precursor solution comprising 50 grams of acetone and 100 grams of methanol.

20 Figure 13 is a graphic illustration of a Raman spectrum for the diamond film of Figure 12.

Figure 14 is an optical micrograph of diamond crystallites grown in accordance with the present invention on a clean and untreated silicon wafer by a

microwave plasma in the vapor of a solution comprising 100 grams of isopropanol and 100 grams of methanol.

Figure 15 is a graphic illustration of a Raman spectrum for the diamond crystallites of Figure 14.

5 Figure 16 is an optical micrograph of diamond crystallites deposited in accordance with the present invention on a clean and untreated silicon wafer by a microwave plasma in the vapor of a precursor comprising isopropanol.

Figure 17 is a graphic illustration of a Raman spectrum for the diamond crystallites of Figure 16.

10 **DETAILED DESCRIPTION OF THE INVENTION**

For a more complete understanding of the present invention, reference should be made to the following detailed description taken in connection with the accompanying figures.

The present invention relates to a method of synthesizing diamond crystals and
15 diamond films for a very broad range of scientific and technological applications such as optical windows, machining tools, heat spreaders, tribological coatings, sensors and actuators, electrochemical coatings, protective coatings, and wide-bandgap semiconductor devices. The method of the present invention uses a premixed methanol-based liquid solution as the feedstock. The methanol-based solution
20 contains 0.5-99.5% by weight of one or more carbon containing compounds with the molar ratio of atomic carbon to atomic oxygen being greater than one. Although water and other compounds that can be dissociated by a plasma to form O, H, F, Cl, Br, and OH radicals may be added to the methanol-based solution, it is not a

requirement for the deposition of diamond crystals and diamond films by the method of the present invention.

Figure 1 generally illustrates the plasma enhanced chemical vapor deposition system utilized in performing the method of the present invention. As illustrated in Fig. 1, the precursor 5 is fed from a precursor container 4 by a conduit 6, such as a TEFLON or metal tubing, through a liquid flow controller 7, such as a needle valve, to an inlet 2 of reactor chamber 1. The reactor chamber 1 is formed from a material capable of withstanding the temperature generated during the CVD process. In the present invention, the reactor chamber 1 is stainless steel and typically 8" in diameter.

When the liquid precursor 5 enters the low pressure side of the liquid flow controller 7, it vaporizes to form a vapor precursor 5 comprising a mixture with the same molar composition as the liquid precursor 5. In addition to inlet 2, the reactor chamber 1 has an outlet 3 connected to a mechanical vacuum pump 13 through an automatically controlled throttle valve 14 to maintain constant pressure in the reaction chamber 1 throughout the deposition process and for circulating the vapor of the precursor 5 through the reactor chamber 1. The vapor precursor 5 is maintained at a pressure within the vacuum chamber 1 of between 1 mtorr and 250 torr, with the pressure being monitored by a pressure gauge (not shown).

Electromagnetic energy 8 discharged at various frequencies, for example, DC, RF, and microwave, and also high frequency electromagnetic energy such as energy discharged from a laser, is applied to the reactor chamber 1. A window 9 such as a quartz window that separates the low pressure reactor from ambient pressure and permit microwave energy to propagate into the reaction chamber 1. Preferably, the

electromagnetic energy 8 is microwave energy. The reactor chamber 1 is a part of the cylindrical cavity for the microwave of 2.45 GHz. A substrate 11 is placed on a substrate holder 12, preferably a water cooled substrate holder to control the temperature of and cool the substrate 11. Substrate 11 temperature is monitored with
5 a dual color optical pyrometer (not shown). The plasma 10 dissociates the vapor precursor 5 and releases OH, H, O, CH₃, CH₂, etc. radicals for a net deposition of diamond on a substrate surface 15. Methanol vapor (CH₃OH) has a carbon to oxygen ratio equal to one. In the present invention, when methanol dissociates, it forms high concentrations of radicals that rapidly etch carbon, including diamond, resulting in
10 slow growth of diamond in areas where a diamond deposition rate exceeds the etching rate. The growth rate and degree of non-uniformity also depend on the exposure of carbon, which may be present in some reactor fixtures or previously coated on reactor walls or the substrate holder, to the methanol plasma.

When the precursor 5 comprises a solution of methanol and a proper quantity
15 of one or more carbon containing compounds having a carbon to oxygen ratio greater than one, diamond growth is substantially uniform, reproducible, and at a higher growth rate than conventional CVD methods. For example, ethanol (CH₃CH₂OH), isopropanol, ((CH₃)₂CHOH), and acetone (CH₃COCH₃) have respective carbon to oxygen ratios of 2, 3, and 4. The selection of the carbon containing compound is not
20 limited to ethanol, isopropanol, or acetone, and may be selected from other such carbon containing compounds having carbon to oxygen ratios greater than one. In addition, as indicated in Example 8 below, under certain CVD conditions, it is not required for the precursor 5 to contain methanol. However, if the precursor comprises

only a carbon containing compound having carbon to oxygen ratios greater than one, suppression of the formation of non-diamond phases can generally be maintained by lowering the substrate temperature to below about 900° C and/or selectively neucleate the substrate with high quality diamond particles. Also, diamond growth is as well a
5 function of the plasma density, reaction chamber pressure, carbon to oxygen ratio at the substrate surface, and precursor flow rate, and these functions must be monitored and adjusted accordingly to promote diamond growth. Further, if it is desired for the diamond to contain a dopant, the carbon containing compound can comprises dopant elements or moieties in addition to C, O, and H, such as boron, phosphorus, silicon,
10 etc. Such dopants include, but are not limited to, halides, metals, and the like. Still further, carrier gasses, such as argon, hydrogen, and the like may be utilized to increase the precursor flow rate into or through the reaction chamber 1.

The substrate can comprise any suitable material conventionally utilized in CVD processes. Useful substrate materials are capable of withstanding the
15 temperatures generated during the plasma process. Examples of such substrates include, but are not limited to, a sheet or wafer of silicon, copper, aluminum, molybdenum, and alloys thereof. Further, the substrate may be either unseeded or seeded with diamond crystallites. Seeding can be accomplished by polishing the diamond growing surface of the substrate with diamond paste containing diamond
20 particles, such as 1 μm particles.

In experiments conducted using the method of the present invention, the deposition process lasted for 2-100 hours resulting in diamond films with well faceted diamond grains clearly visible using an optical microscope. The diamond grain sizes

range from sub-micrometers to more than 500 μm .

An electromagnetic, such as microwave, plasma enhanced chemical vapor deposition technique using a precursor comprising methanol-based solutions or a carbon containing compound having a carbon to oxygen ratio greater than one as the feedstock has been developed for the deposition of diamond crystals and diamond films. The CH, H, O radicals generated by the dissociation of the precursor vapor are shown to be sufficient in suppressing the growth of graphitic and amorphous carbon, which results in the net deposition of diamond by the carbon containing radicals that were dissociated from the same vapor. By the addition of carbon containing compounds having a carbon to oxygen ratio greater than one to methanol, the diamond growth rate increases by orders of magnitude over conventional methods.

The aforementioned precursors are less costly than the typical compressed gases that are often used for diamond deposition. Further, the mixing of a methanol-based solution can be performed under standard conditions without the need for an expensive precision electronic mass flow controller.

In contrast to what was reported by *Buck*, who deposited clusters of diamond crystallites in a small area of 3-4 mm^2 in a methanol plasma, when methanol was used alone as the precursor feedstock for substrates of 25 mm x 25 mm in size or larger, only the area near the edge showed acceptable diamond nucleation density in some cases. The diamond deposition was highly non-uniform across the substrate surface. In other cases, too much oxidizing and carbon etching radicals were generated in the methanol plasma resulting in a very slow growth of diamond. For example, when 2,000 W microwave was applied at a pressure of 80 torr and a substrate temperature

of 900° C, the methanol plasma deposited only about 2 µm diamond on a molybdenum substrate after 40 hours of deposition. The diamond growth rate is only 0.05 µm per hour in this case. Using a solution comprising of methanol and one or more carbon containing compounds, that have carbon to oxygen ratio being greater than one, diamond deposition rates of more than two orders of magnitude have been achieved in the present invention.

EXAMPLES

A. Substrate pre-treatment and cleaning.

Substrates of silicon, aluminum, and molybdenum were cleaned by acetone and methanol before being loaded onto the substrate holder. Except those substrates specified to be untreated, all substrates were polished with diamond paste containing 1 µm sized diamond particles.

B. Deposition parameters.

Typical deposition parameters are as follows:

Microwave power	600-3000W
Vapor pressure	1 mtorr-250 torr
Substrate temperature	300° C-1600° C
Methanol	0.5-99.5% by weight
Ethanol, isopropanol, and acetone	0.5-99.5% by weight

C. Diamond film characterization methods.

A Normaski phase contrast optical microscope was used to examine the crystal shapes and surface morphology of the deposited films. Diamond grains with

100 or 111 facets can clearly be seen using this optical microscope. The diamond film thickness can also be measured by examining the cross-sectional view of such films using the same optical microscope. A micro Raman spectrometer powered by an Argon ion laser was used to examine the phase purity of the deposited films.

- 5 Diamond peak around 1332 cm^{-1} provided convincing evidence that the deposited carbon films were diamond.

The following examples are provided to illustrate the present invention but are not to be construed as limiting the invention in any way.

Example 1

- 10 A liquid solution comprising 4.6 grams of ethanol and 100 grams of methanol was used as the precursor feedstock. A molybdenum plate of 1/2 inch thick and 2 inches in diameter was polished by diamond paste containing $1\text{ }\mu\text{m}$ sized diamond powder and cleaned by acetone and methanol. Microwave power of 2kW was applied at the vapor pressure of 80 torr resulting in the substrate being heated to $1,000^{\circ}\text{C}$.
- 15 After 45 hours of deposition, the film separated itself from the molybdenum substrate and was of about $45\text{ }\mu\text{m}$ in thickness. The growth rate was about $1\text{ }\mu\text{m}$ per hour. Diamond growth rate increased with increasing quantity of ethanol in the methanol-based solution. Figure 2 shows the optical micrograph of the free-standing diamond film. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 3
- 20 indicates that the diamond film is of very good quality.

Example 2

A liquid solution comprising 4 grams of isopropanol and 100 grams of methanol was used as the precursor feedstock. A molybdenum plate of 1/2 inch thick

and 2 inches in diameter was polished by diamond paste containing 1 μm sized diamond powder and cleaned by acetone and methanol. Microwave power of 2kW was applied at the vapor pressure of 80 torr resulting in the substrate being heated to 1,000° C. After 22 hours of deposition, the film separated itself from the

5 molybdenum substrate and was of about 44 μm in thickness. The growth rate was about 2 μm per hour. Figure 4 shows the optical micrograph of the free-standing diamond film. The clear diamond peak in the Raman spectrum shown in Figure 5 indicates that the diamond film is of good quality.

Example 3

10 A liquid solution comprising 3.5 grams of acetone and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a water cooled molybdenum holder. The silicon wafer was polished by diamond paste containing 1 μm sized diamond powder and cleaned by acetone and methanol before loading onto the substrate holder. Microwave power of 2kW was applied at the vapor

15 pressure of 60 torr resulting in the substrate being heated to 1030° C. After 23 hours of deposition, the diamond film was about 30 μm in thickness. The growth rate was about 1.3 μm per hour. Figure 6 shows the optical micrograph of the diamond film on silicon. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 7 indicates that the diamond film is of good quality.

20 Example 4

A liquid solution comprising 15 grams of acetone and 100 grams of methanol was used as the precursor feedstock. An aluminum plate of 2" diameter was placed on a water-cooled molybdenum holder. The aluminum plate was polished by diamond

paste containing 1 μm sized diamond powder and cleaned by acetone and methanol before loading onto the substrate holder. Microwave power of 650 W was applied at a vapor pressure of 11 torr, resulting in the substrate being heated to 535° C. After 5 hours of deposition, the microwave power was increased to 800 W, and the vapor pressure was increased to 16 torr for another 5 hours of deposition at 613° C. A continuous diamond film was coated onto the aluminum plate with good adhesion. Figure 8 shows the optical micrograph of the diamond film on aluminum. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 9 indicates that the coating was indeed a diamond film.

10 Example 5

A liquid solution comprising 50 grams of acetone and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a water-cooled molybdenum holder. The silicon wafer was cleaned by acetone and methanol but not polished by diamond paste before loading onto the substrate holder. Microwave power of 1,100 W was applied at a vapor pressure of 35 torr, resulting in the substrate being heated to 724°C. After 2 hours, diamond nucleated and grew to the size of about 4 μm . The growth rate was about 2 μm per hour. Figure 10 shows the optical micrograph of the diamond crystallites on the untreated silicon wafer. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 11 indicates that the diamond crystallites are of good quality.

Example 6

A liquid solution comprising 50 grams of acetone and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a

water-cooled molybdenum holder. The silicon wafer was polished by diamond paste containing 1 μm sized diamond powder and cleaned by acetone and methanol before loading onto the substrate holder. Microwave power of 1,100 W was applied at a vapor pressure of 29 torr, resulting in the substrate being heated to 800° C. After 4
5 hours of deposition, a diamond film was deposited. Figure 12 shows the optical micrograph of the diamond film on silicon. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 13 indicates that the diamond film is of good quality. In addition to the diamond peak, the Raman spectrum shows another broad band around 1550 cm^{-1} indicating the inclusion of non-diamond phases in the diamond
10 grains, in the grain boundaries, or in both.

Example 7

A liquid solution comprising 100 grams of isopropanol and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a water-cooled molybdenum holder. The silicon wafer was cleaned by
15 acetone and methanol, but not polished by diamond paste, before loading onto the substrate holder. Microwave power of 1kW was applied at a vapor pressure of 36 torr, resulting in the substrate being heated to 754° C. After 2 hours and 40 minutes, diamond nucleated and grew to the size of about 7 μm . The growth rate was about 2.7 μm per hour. Figure 14 shows the optical micrograph of the diamond crystallites on
20 the untreated silicon wafer. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 15 indicates that the diamond crystallites are of good quality.

Example 8

Substantially pure isopropanol was used as the precursor feedstock. A silicon

wafer of 1" x 1" in size was placed on a water-cooled molybdenum holder. The silicon wafer was cleaned by acetone and methanol, but not polished by diamond paste, before loading onto the substrate holder. Microwave power of 900 W was applied at a vapor pressure of 30 torr, resulting in the substrate being heated to 740° C. After 2 hours and 14 minutes, diamond nucleated and grew to the size of about 2 μm . The growth rate was about 1 μm per hour. Figure 16 shows the optical micrograph of the diamond crystallites on the untreated silicon wafer. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 17 indicates that the crystallites are indeed diamond. The much stronger background signal and the higher broad band near 1550 cm^{-1} in the Raman spectrum shown in Figure 17 as compared to those shown in Figure 15 indicate that the quality of the diamond crystallites was improved by the addition of methanol to isopropanol.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

WHAT IS CLAIMED IS:

1. A method of forming diamond crystals or a diamond film comprising:
disposing a substrate in a reaction chamber; and
subjecting a vaporized precursor comprising at least one carbon containing compound having a carbon to oxygen ratio greater than one to a plasma under conditions effective to dissociate the precursor and promote diamond growth on the substrate.
2. The method according to claim 1, wherein the precursor comprises a solution of methanol and the at least one compound having a carbon to oxygen ratio greater than 1.
3. The method according to claim 2, wherein methanol is present in the precursor in an amount between about 0.5 wt.% to about 99.5 wt. % of the precursor.
4. The method according to claim 1, wherein the precursor is selected from the group comprising of ethanol, isopropanol, acetone, and combinations thereof.
5. The method according to claim 1, wherein the precursor is a solution of methanol and a compound selected from the group comprising of ethanol, isopropanol, acetone, and combinations thereof.
6. The method according to claim 1, wherein the subjecting a vaporized precursor step is conducted at a pressure between about 1mtorr and 250 torr.
7. The method according to claim 1, wherein the substrate is heated to a temperature between 300° C to about 1,600° C.
8. The method according to claim 1, wherein the carbon containing

compound further comprises a dopant element or moiety.

9. The method according to claim 1, wherein the substrate comprises a sheet or wafer of silicon, copper, aluminum, molybdenum, or alloys thereof.

10. The method according to claim 1, wherein the plasma is induced by electromagnetic energy.

11. The method according to claim 10, wherein the electromagnetic energy has a frequency selected from the group comprising of direct current, radio frequency, and microwave.

12. The method according to claim 1, wherein the plasma is induced by microwave energy.

13. A plasma enhanced chemical vapor deposition of diamond crystals and diamond films on surfaces of a substrate comprising:

providing an apparatus including an inlet, a dissociation zone, a deposition zone and an outlet;

introducing a precursor comprising methanol and at least one carbon containing compound containing a carbon to oxygen ratio greater than one into the inlet under conditions effective to vaporize the precursor, flow the precursor through the dissociation zone, and through the outlet;

dissociating and reacting the vaporized precursor as vaporized precursor flows or diffuses through the dissociation zone to produce OH, H, O, and carbon containing radicals; and

transporting the radicals to the substrate in the deposition zone to produce the diamond crystals or diamond films on the surface of the substrate.

14. The process according to claim 13, wherein the dissociation and reacting steps comprise:

passing the vaporized precursor through an electrical discharge zone for dissociating the precursor in the dissociation zone.

15. The process according to claim 13, wherein the introducing step comprises:

introducing the liquid precursor with methanol in an amount between about 0.5 wt.% and about 99.5%.

16. The process according to claim 15, further comprising:
supplementing methanol with one or more carbon containing compounds containing carbon, hydrogen, and oxygen with the atomic ratio of carbon to oxygen greater than one.

17. The process according to claim 16, further comprising:
selecting the supplementing compounds from the group comprising of ethanol, isopropanol, acetone, and combinations thereof.

18. The process according to claim 13, wherein the deposition zone is maintained at a temperature between about 200° C to 1600° C and at a pressure between 1 mtorr and 250 torr.

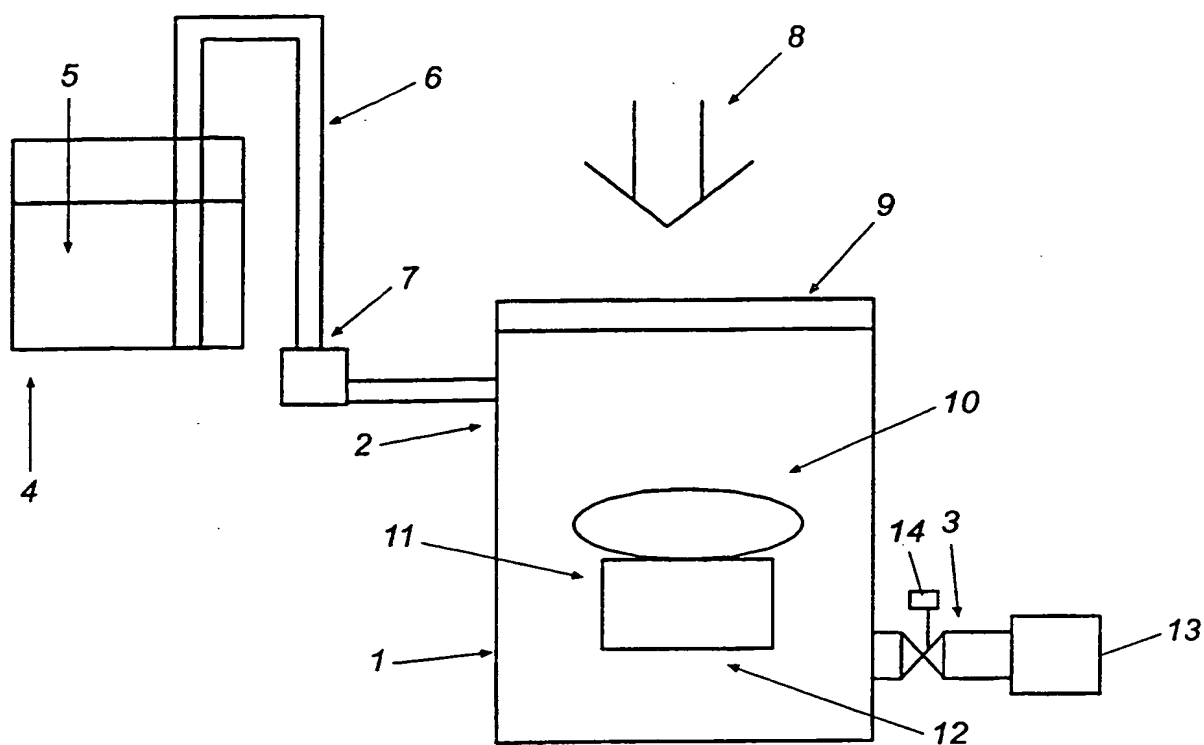
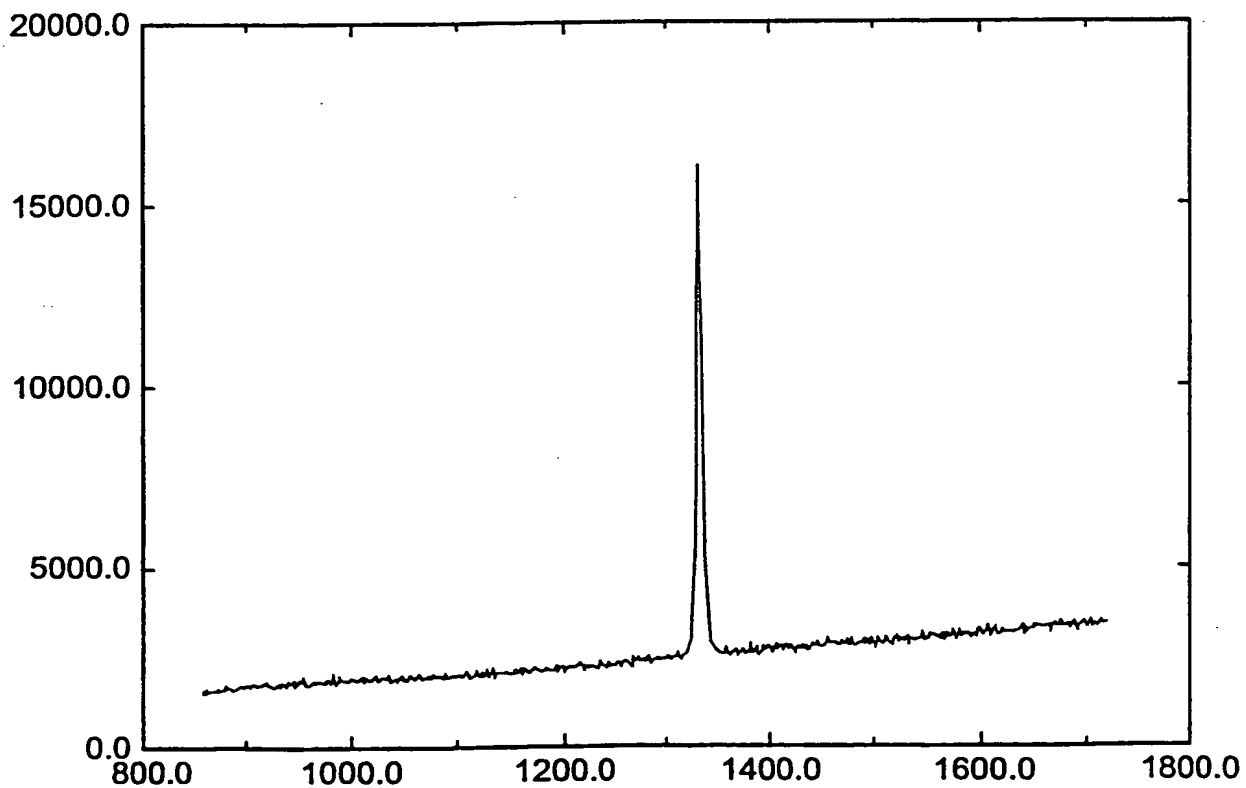
**Fig. 1****Fig. 3**



Fig. 2

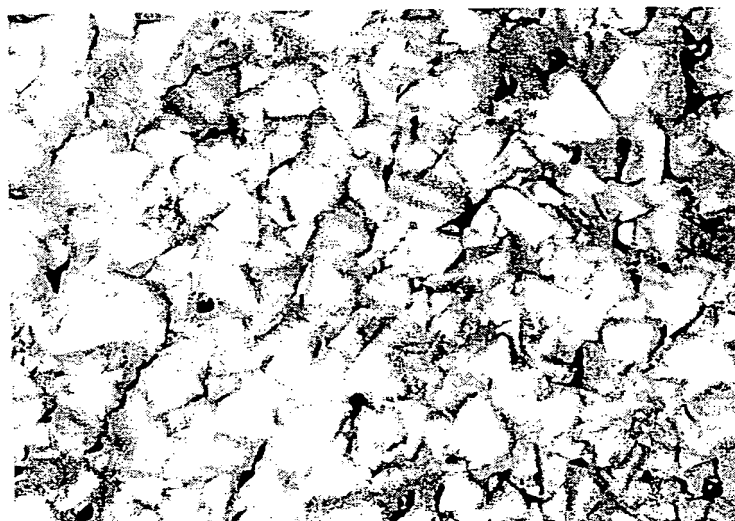


Fig. 4

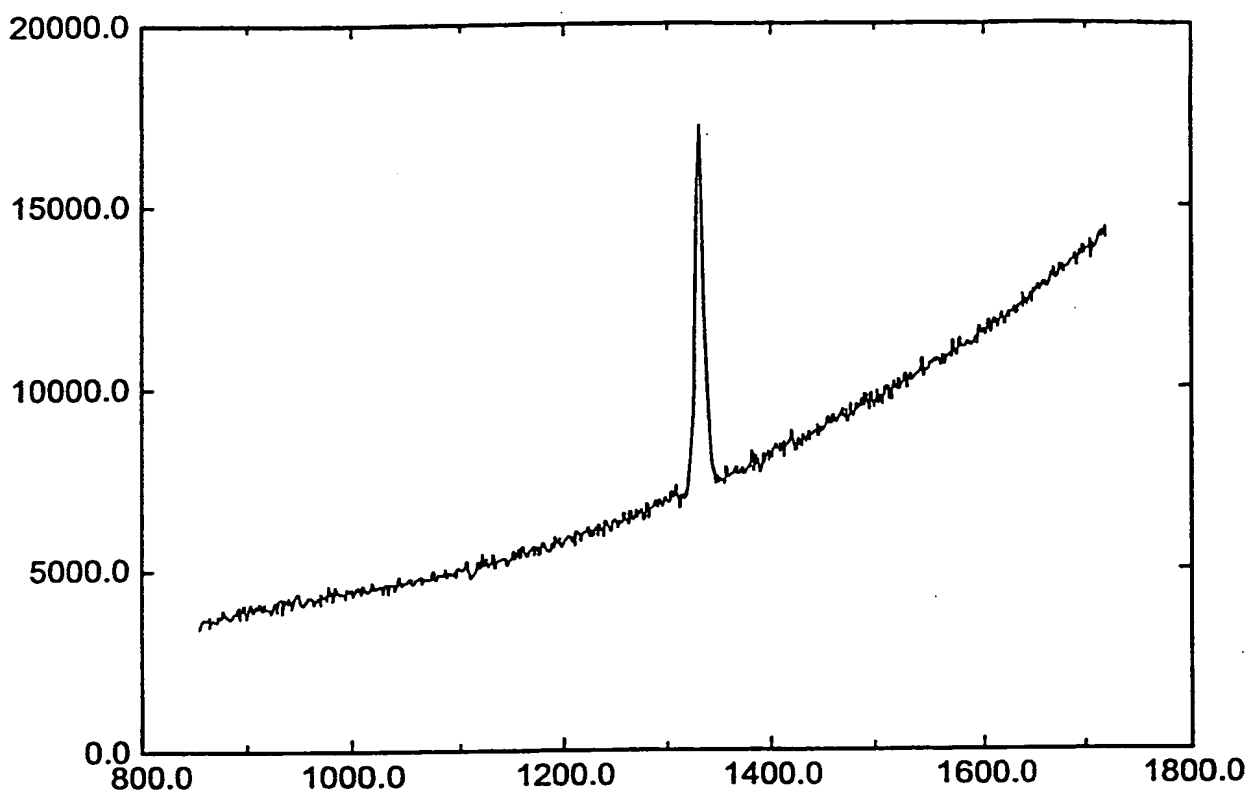
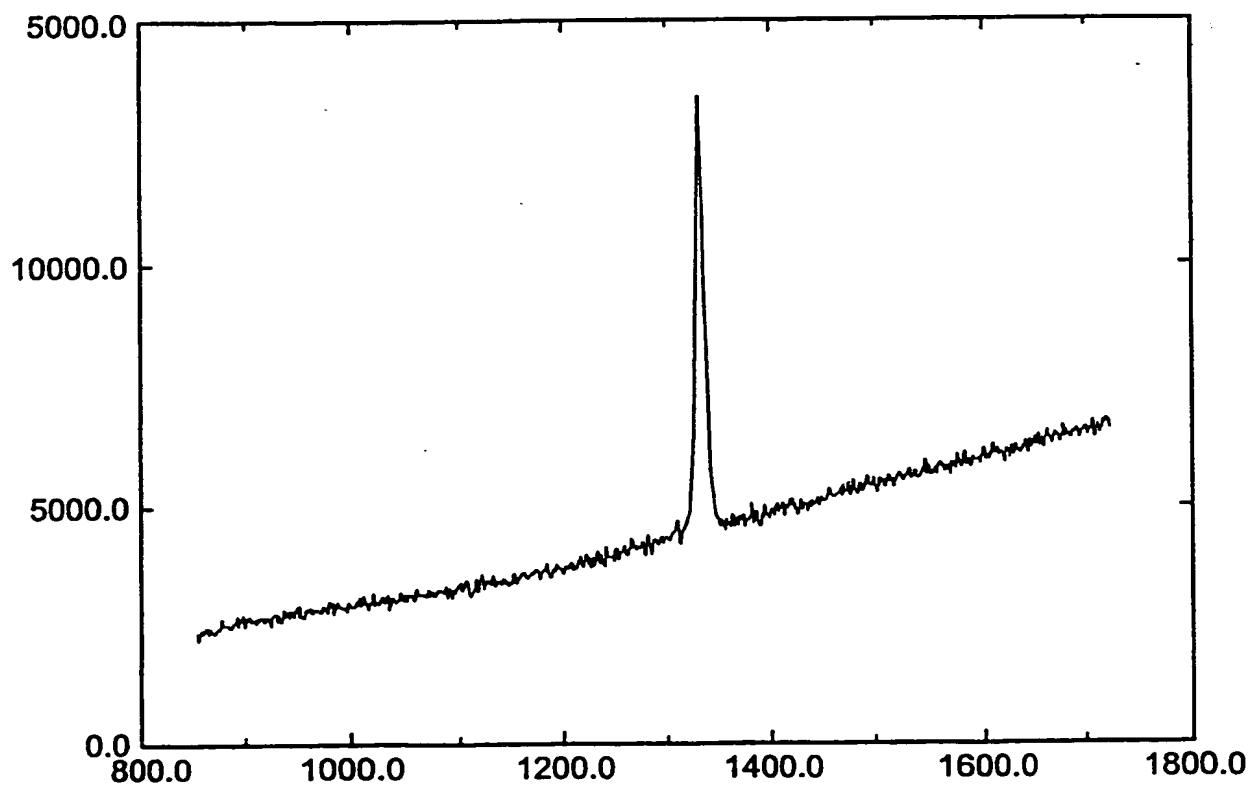
***Fig. 5******Fig. 7***



Fig. 6

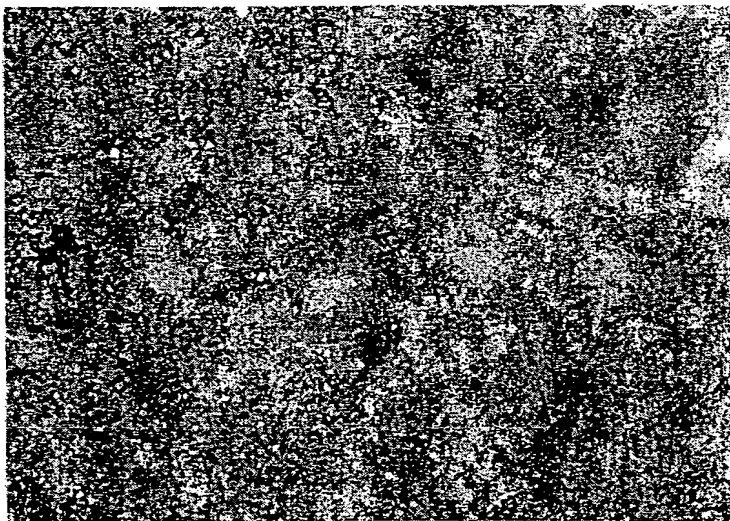
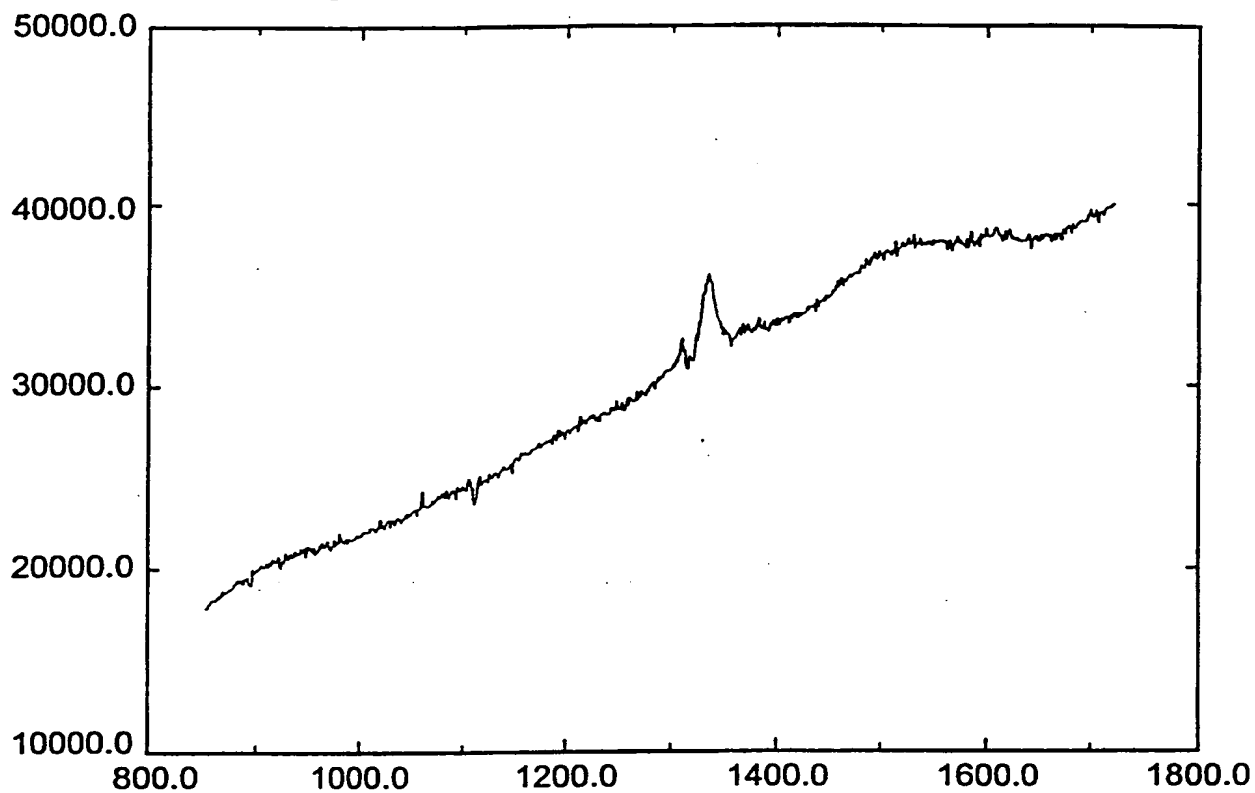
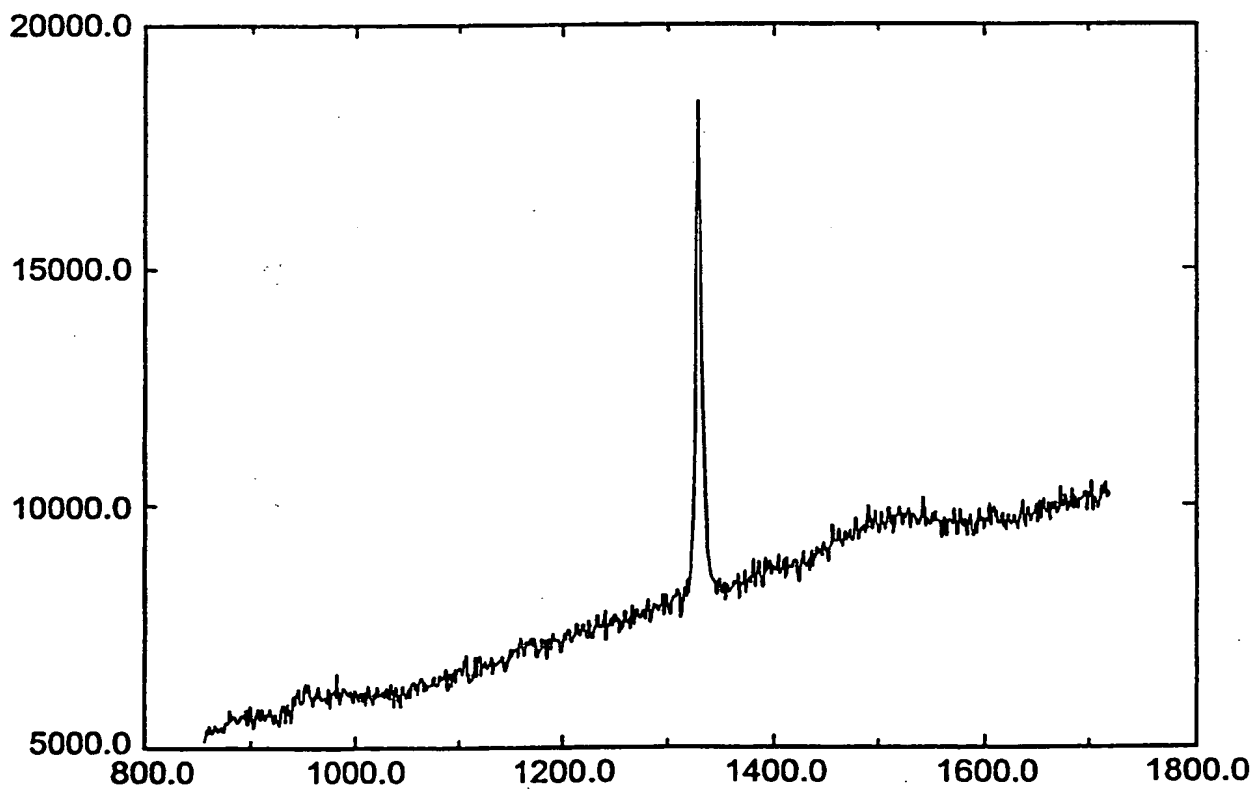


Fig. 8

**Fig. 9****Fig. 11**

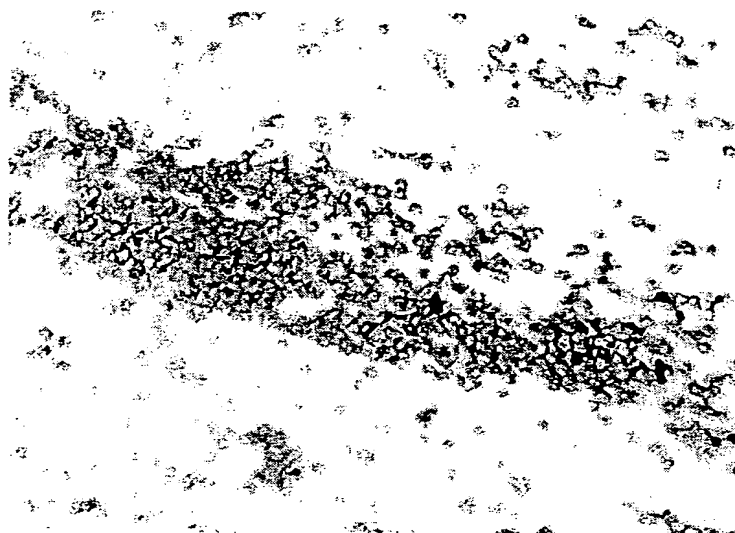


Fig. 10

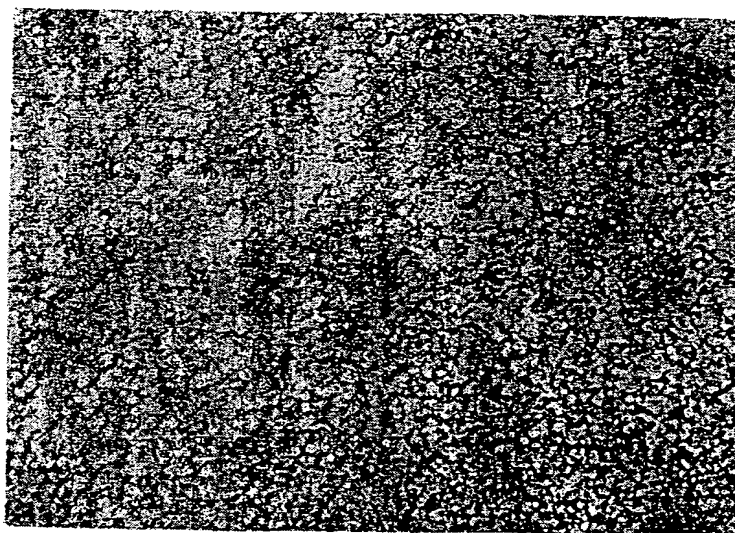
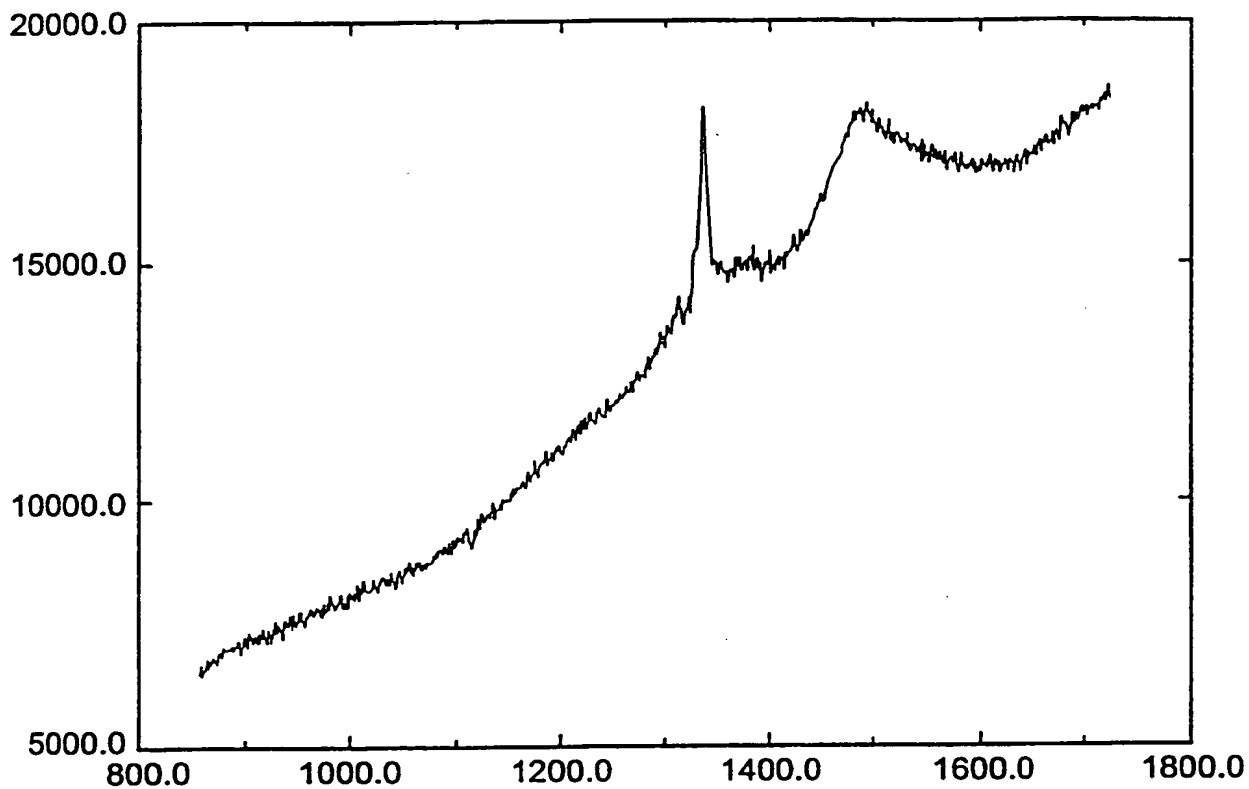
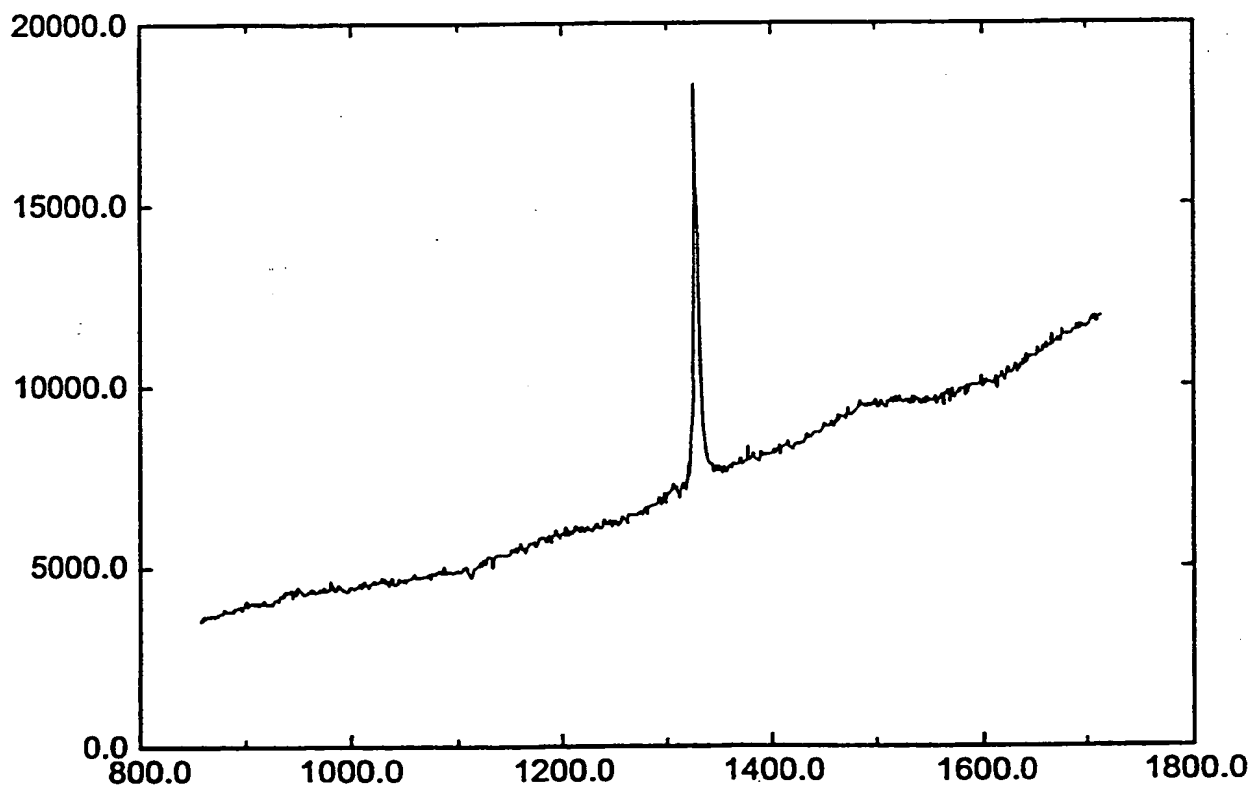


Fig. 12

**Fig. 13****Fig. 15**

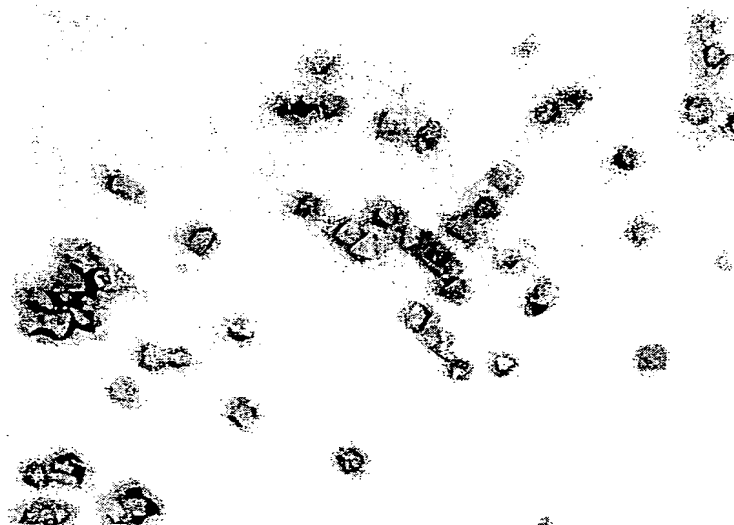


Fig. 14

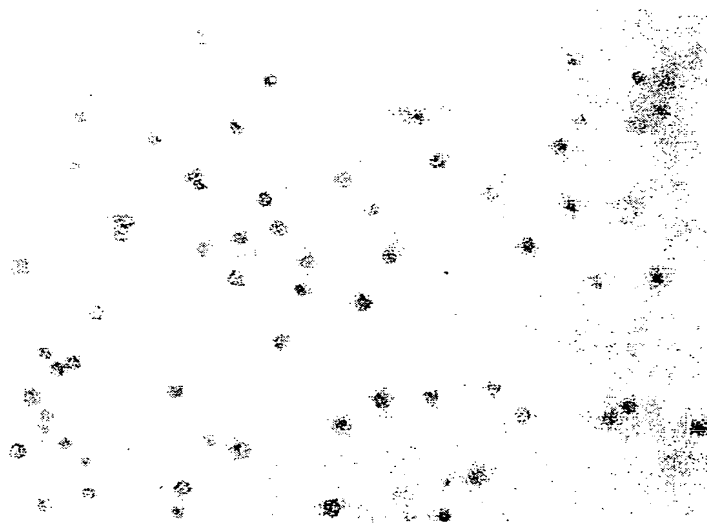
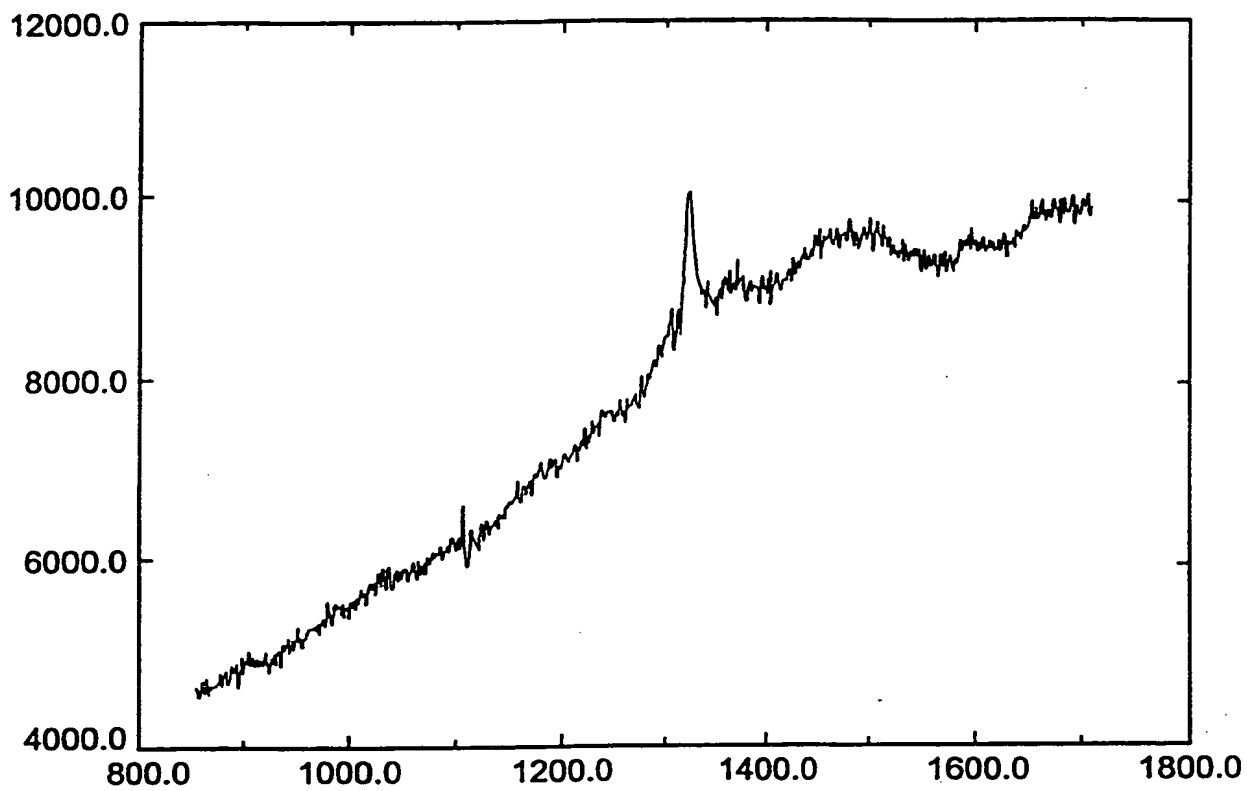


Fig. 16

***Fig. 17***

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03502

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H05H 1/24; C23C 16/26

US CL :427/577, 249.8, 575; 423/446

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/577, 249.8, 575; 596: 423/446

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
'STN', 'West'

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
'diamond', 'plasma', 'CVD', 'methanol'

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	SINGH et al, ' Low-pressure, low-temperature, and remote-plasma deposition of diamond thin films from water-methanol mixtures', Appl. Phys. lett. 61(24), 14 December 1992, pages 2863-2865.	1,6,7,9-12 ----- 2-5, 8, 13-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

08 JUNE 2000

Date of mailing of the international search report

05 JUL 2000

Name and mailing address of the ISA/US
Receiving Office (as published in the PCT Gazette, January 1998)*
Box PCT

Authorized officer
Telephone No. (703) 308-1146

DEBORAH THOMAS
PARALEGAL SPECIALIST

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)